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Field Emission from Multiwalled Carbon Nanotubes Prepared by Chemical Vapor Deposition using Fe-phthalocyanine as Starting Material

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Carbon nanotubes (CNTs) have strongly attracted many researchers' and developers' attension since their descovery [1]. Because of their chemical stability, mechanical stiffness and high aspect ratio, many applications are expected such as anode for Li-ion battery [2], hydrogen strage [3], field emissoin cathode and so on. Field emission cathode is a one of the most promising applications of CNTs. Current-voltage characteristics of field emission was studied by R. H. Fowler and L. W. Nordheim [4]. They expressed them with following relation, $I = AF^2exp(-B/F)$, Fowler-Nordheim relation, where I and F are emission current and local electric field near the emitting surface. The A and B are constant. In 1995, Rinzler et al. reported the field emission from a multiwalled carbon nanotube (MWCNT) [5]. In same year, de Heer et al. prepared vertically aligned MWCNTs and observed field emission from it [6]. Since these reports, many experimental studies on field emission from CNTs have been reported [7,8].

In this study, we have realized the field emission from MWCNTs and observed shift of onset voltage of the emission current toward the higher side. Furthermore, we found increase of the emission current and field enhancement factor after a 120 h running. We report these current-voltage characteristics of MWCNTs and discuss on them.

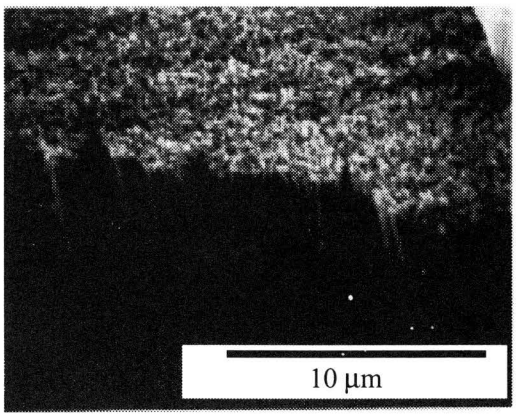

Fig. 1. SEM images of MWCNT mat prepared by CVD on quartz plate with Au/Cr film contacts.

The MWCNTs ware prepared by chemical vapor deposition (CVD) on a quartz plate with Au/Cr film contacts under high vacuum or H_2/Ar gas flow. The Au/Cr film contacts ware formed by vacuum deposition and had a shape of comb teeth with 120 μm width strips and 80 μm gaps. CVD was performed at 850°C under a H_2/Ar mixture gas flow at a rate of 30/30 mm^3/min. The details and development of CVD is described in Ref. [9-12].

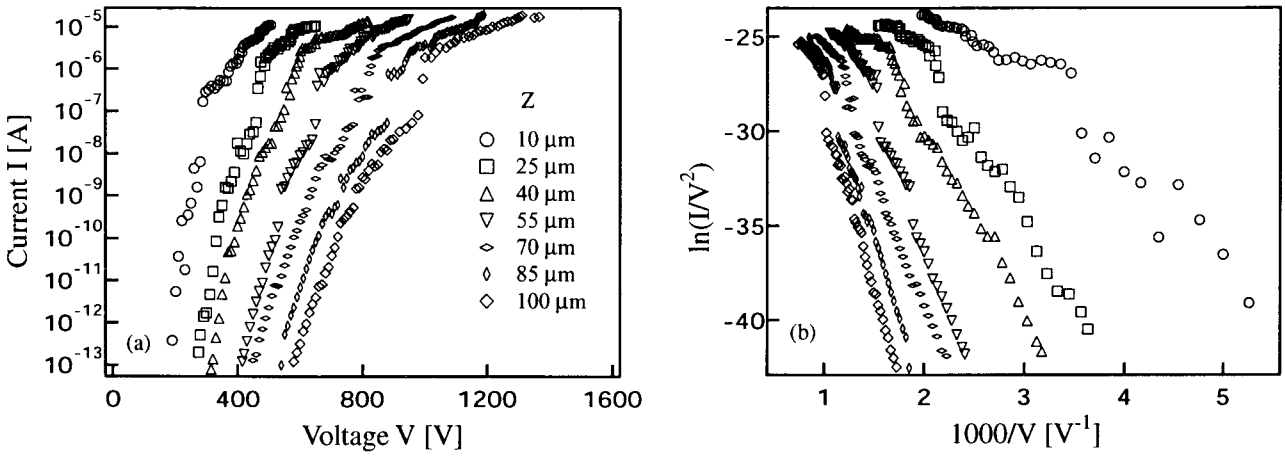

Fig. 2. (a) Current-voltage characteristics of field emission from MWCNT mat and (b) FN plot the data shown in (a).

Figure. 1 shows a scanning electron microscope (SEM) image of our sample. We estimated the MWCNT density at 1.6×10^{13} tubes/m^2. The diameter of the tip of a MWCNT was 20-60 nm and its length was 5 μm.

We performed field emissoin measurement in a vacuum chamber with a 6×10^{-8} Torr base pressure. We used a tungsten probe with a diameter of 500 μm as an anode. The cross-sectional area of the anode was 1.96×10^{-7} m^2.

Figure 2(a) shows the current-voltage characteristics of MWCNTs measured for various z which is distance between the anode and the MWCNT tip. The onset voltage of emission current moved toward the higher side with increasing z. This is different from single metal emitter whose onset voltage does not move with z. The increase of onset voltage results from disturbing the penetration of electric field into MWCNTs because of dense growth of them. Fig. 2(b) shows FN plot of the data shown in Fig. 2(a). The field enhancement factor β was estimated to be 140 - 400 at $z = 10 - 100\mu$ m. The β is defined as follows. $F = \beta\langle F\rangle$ where the F is local field near the tip of MWCNT and the $\langle F\rangle$ is macroscopic electric field between the tungsten probe and the MWCNT tip.

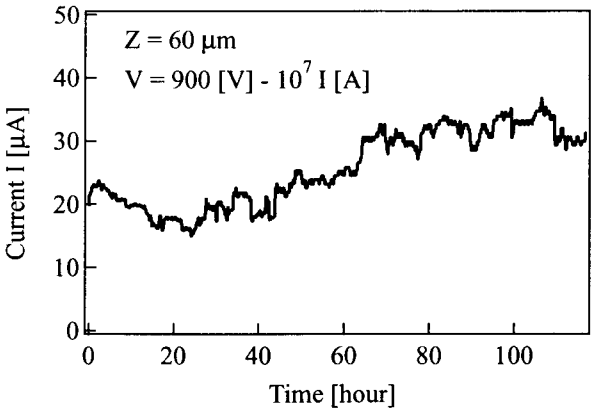

Fig. 3. Time dependence of emission current of 120 h runnning.

We ran the device over 120 h. It was initially set in relatively high current (20 μA)-voltage (700 V) running condition for $z = 60$ μm. Figure 3 shows the time dependence of emission current from 0 h to 120 h. During the initial 20 h, emission current was reduced to 15 μA. And then, it was gradually increased to about 30 μA which was 1.5 times higher than initial current

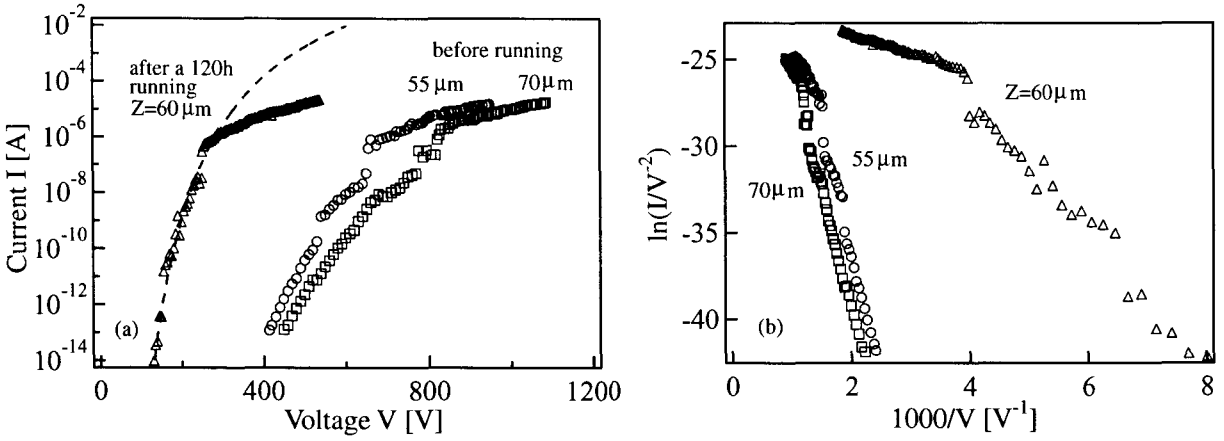

Fig. 4. (a) Current-voltage characteristics before and after 120 h running. (b) FN plot of the data shown in (a). The dashed line is FN fitting to the low voltage regime.

level in spite of lower applied voltage 600 V.

Figure 4 shows the current-voltage characteristics before and after 120 h runnning and their FN plots. The onset voltage was drastically lowered from 400 V to 125 V, and the field enhancement factor β increased from 360 to 1110 by a 120 h running. This indicates occurrence of geomatrical change such as opening of MWCNT cap caused by residual gas ion bomberding and rearrangement of carbon atom at the tip of dome-closed cap due to current-induced heating effects.

As can be seen in Fig. 4(a) current saturation occured. The potential drop reached 240 V (40 % of bias voltage 600 V) and reduce the emission current by two orders of magnitude. We found that the current saturation occured at constant local electric field $F_{knee} = 4 \times 10^3$ V/μm without dependence of z before and after 120 h running. This saturation is caused by penetration of electric field into MWCNTs.

In conclusion, we prepared MWCNTs on quartz plate with Au/Cr film contacts by CVD using Fe-phthalocyanine as source material. We demonstrate field emission from MWCNTs and observed a movement of onset voltage toward higher side with increasing z. By running for 120 h, onset voltage was dorastically lowered and field enhancement factor β was increased. The average current density of this emitter was 10 mA/cm^2 at a bias voltage 600 V for $z = 60$ μm. The above results were reproducible for multiple samples. For flat panel display applicatoin, the current density of 1 mA/cm^2 is required, so this emitter promises this application.

Acknowledgemnt

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